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Characterizing the solid–solution partitioning coefficient and plant uptake factor of As, Cd, and Pb in California croplands

Weiping Chen [a,b,*], Lianqing Li [c], Andrew C. Chang [b], Laosheng Wu [b], Rufus L. Chaney [d], Richard Smith [e], Husein Ajwa [f]

[a] State Key Lab of Urban and Regional Ecology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] Department of Environmental Sciences, University of California, Riverside, CA 92521, United States
[c] Institute of Resources, Ecosystem and Environment of Agriculture, Nanjing Agricultural University, Nanjing 210095, China
[d] Environmental Management and Byproduct Utilization Laboratory, USDA ARS, Beltsville, MD, United States
[e] University of California Cooperative Extension, Monterey County, CA, United States
[f] Department of Plant Sciences, University of California, Davis, CA, United States

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ABSTRACT

In risk assessment models, solid–solution partition coefficient, K_d, and plant uptake factor, PUF, are often employed to depict the fate and transport of trace elements in soils. The trustworthiness of risk assessments depends on the reliability of the parameters used. In this study, we examined K_d and PUF for As, Cd and Pb based on soils and plant tissues obtained from 70 crop production fields in California. We also examined the California portion of a nationwide survey of trace elements in cropland soils conducted by the Soil Survey, Natural Resources Conservation Service, USDA. Results showed that the K_d and PUF for cropland soils are probabilistic in nature and follow log-normal distributions. The trace element concentration of the soil solution did not appear to be a more appropriate estimator of PUF than the total soil element content. The K_d used in the CDFA (California Department of Food and Agriculture) study had a much wider range than that could occur in California croplands while the PUF used in the CDFA risk assessment was comparable to patterns observed in the field measurements.

1. Introduction

Trace elements such as As, Cd, and Pb may inadvertently be added to cropland soils through atmospheric fallouts and anthropogenic inputs of fertilizers, irrigation water, and other amendments (Chang and Page, 2000). Their accumulation in cropland soils poses a potentially serious threat to human and ecosystem health (de Meeus et al., 2002; Hinwood et al., 2004). To ensure that trace element levels in crops produced for human consumption do not cause unacceptable risks to the consumer health, regulatory authorities have established numerical limits for nonnutritive elements in fertilizers and other soil amendments based on outcomes of risk assessments (McGrath et al., 1994; Chen et al., 2007a).

The efficacy of risk assessments depends on reliability of parameter values employed in the computations. Customarily, the food chain transfer of potentially toxic trace elements such as As, Cd and Pb, from their environmental releases to soils and then to crop plants, is characterized by first estimating their soil solution concentration via a solid–solution partition coefficient (K_d). The same amounts of trace element in the solid phase of soils however do not necessarily result in the same concentrations in solution phase. The parameter K_d normalizes the mineralogical and chemical differences of soils and expresses the trace element of the soils in the soluble form that is the biologically reactive portion of the total pool. Mathematically, the solid–solution partition coefficient is defined in a linear form as:

$$K_d = \frac{C_{total}}{C_{soil\,solution}} \quad (1)$$

where C_{total} (mg kg^{-1}) and $C_{soil\ solution}$ (mg l^{-1}) refer to the total and solution concentration of a trace element in soil, respectively, given K_d the unit of l kg^{-1}. To determine the partition of trace elements between the solid and solutions phases, batch adsorption

* Corresponding author at: Department of Environmental Sciences, University of California, Riverside, CA 92521, United States. Tel.: +1 951 827 3892; fax: +1 951 827 5295.
E-mail address: chenweip@yahoo.com.cn (W. Chen).

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experiments are frequently employed (Butcher et al., 1989; Jopony and Young, 1994; Sauve et al., 2000). Conceptually, this parameter should be a constant for a given soil. The resulting K_d however is subject to fluctuation according to the soil-to-water ratios employed in the determinations. Chen et al. (2007b) reported that the soil-to-water ratio of 1:0.5 (w/v) mimicked the moisture contents of typical field soils and the K_d based on this soil-to-water ratio were the most consistent.

In crop production systems, trace elements such as As, Cd, and Pb are introduced into soil primarily through applications of phosphate fertilizers and micronutrient supplements. However, the amounts of As, Cd, and Pb that cropland soils may receive are considerably less than those accumulated in soils due to contaminations by industrial emissions and/or accidental spills (Sauve et al., 2000; Krage, 2002). The K_d values of the polluted soils as reported in the published literature may not be representative of the K_d values of the cropland soils receiving trace elements through inorganic fertilizer application because trace elements concentrations in the polluted soils are considerably higher and the mineralogical and chemical characteristics of trace elements in fertilizer ingredients are different from those of the pollutants.

The plant uptake factor, PUF, is comparable to the more commonly adopted term of bioaccumulation factor that depicts the pollutant absorbed by the exposed biota in its habitat notably the aquatic ecosystems. Similarly, PUF which denotes the transfer of trace elements from soil to plant tissue that under steady state is the ratio of the concentration of an element in plant tissue to that in soils (PUF_{total}) or in soil solution ($PUF_{solution}$)

$$PUF_{total} = \frac{C_{plant}}{C_{total}} \tag{2a}$$

or

$$PUF_{solution} = \frac{C_{plant}}{C_{soil\,solution}} \tag{2b}$$

where C_{plant} is the plant tissue concentration of the element (mg kg^{-1}).

Plant uptake of trace elements is a dynamic process and is influenced by soil and season related factors (McBride, 2002; Adams et al., 2004; Huang et al., 2004; Kuo et al., 2004; Koo et al., 2006). Foods coming from various sources are intermingled in the market places and in food acquisition the consumers typically have no knowledge of their origin. In terms of exposure, differences in plant uptake caused by these factors are simply temporal and spatial variability due to production fields where the crops come from (Chen et al., 2008). In risk assessments, the PUF needs to reflect the realities of crop production and consumption patterns.

Both K_d and PUF are attributes that would normalize the differences caused by soils characteristics thus standardize the assessments of human exposure to trace element in the croplands. It is imperative that the K_d and PUF for potentially toxic trace elements in cropland soils be systematically characterized with realistic data obtained from the crop production fields.

When California Department of Food and Agriculture (CDFA) selected the risk-based assessment to evaluate the adverse effects of potentially toxic trace elements in fertilizers (CDFA, 1998), the PUF_{total} instead of $PUF_{solution}$ were employed to estimate the transfer of As, Cd, and Pb from soils to plants. As the uptake is primarily through those present in the soil solution, the total element content of the soil is often considered a less ideal estimator of the element's plant availability in the soils. Again, field-based observations are essential to deduce whether PUF thus the plant tissue accumulation of trace elements would be more appropriately be a function of the dissolved element in soil solution (i.e. $PUF_{solution}$) or total elemental content of the soil (i.e. PUF_{total}).

In this study, we characterize the K_d and PUF of As, Cd, and Pb of California croplands in probabilistic terms; determine the most ideal estimator of PUF – trace element concentration of the soil or soil solution; and evaluate the efficacy of K_d and PUF from which the California's numerical limits for As, Cd, and Pb in fertilizers were based.

2. Material and methods

2.1. Sample collection

Soil and leaf tissue samples were collected from 70 vegetable fields in Oxnard/Ventura Area, and Santa Maria/San Luis Obispo Valley, CA. In terms of trace element inputs, the vegetable fields represented a worst-case scenario because they receive high inputs of phosphorus fertilizers and are continuously cropped. The soil samples were extracted from the 0 to 20 cm deep section representing the plow layer in which the applied fertilizers were incorporated. At each vegetable field, five samples were taken with a 5-cm bucket auger. Each of the five samples was a composite of 4–5 sub-samples that were taken 2 m apart along a straight line transect. The unincorporated organic debris deposited on the soil surface if any was excluded. The composite was field screened to pass a non-metallic screen with 1 mm openings and approximately 500 g of screened soil were gathered and stored. After air-drying, a sub-sample of each was ground with a porcelain mortar and pestle to pass a 200-mesh (75 μm) sieve, and dried overnight at 105 °C prior to analysis.

It is well known that the plant uptake of metals as well as their distribution among different tissues varies greatly between species. For risk assessment and comparison purpose, the leaf tissue was chosen to standardize the plant parts analyzed. Corresponding leaf tissue samples of vegetable crops including bean, bell pepper, broccoli, cauliflower, celery, lettuce, Napa, and spinach were taken at the same locations where soils samples were taken. The leaf tissue samples were washed with dilute non-ionic detergent solution, rinsed with tap water and finally rinsed with de-ionized water, dried at 65 °C for 48 h, ground to pass a screen with 0.1 mm openings, and stored.

2.2. Laboratory analysis

The soil samples were microwave digested according to the modified U.S. EPA Method 3052 using a CEM Mars 5 microwave system equipped with HP-500 Plus pressurized digestion vessels and perfluoro alkoxy ethylene liners (Wei et al., 1997; Link et al., 1998). An aliquot of 0.25 g soil was combined with 9.0 ml HNO_3, 4.0 ml HF and 1.0 ml of de-ionized water in a HP-500 Plus pressurized digestion vessels and PFA (perfluoro alkoxy ethylene) liners for digestion using a CEM Mars 5 microwave system set for the temperature to rise up to 180 ± 5 °C within the 5.5 min and to hold at that temperature for the remaining 9.5 min. Afterwards, the vessels were allowed to cool down in a freezer for 15–20 min and then the solutions were quantitatively diluted to 25 ml with 1% (v/v) optima nitric acid, and stored until the analyses were done. For plant tissue analysis, 0.5 g of ground plant tissue sample mixed with 4.0 ml HNO_3, 4.0 ml H_2O_2 and 2.0 ml of de-ionized water was microwave digested with the same temperature programming as previously described. To verify the accuracy of the sample digestion, standard reference materials (NIST SRM 2709 for soil sample digestion and NIST SRM 1547 for plant tissue sample digestion) were analyzed along with every batch of digestion. The detection limit is 0.5 ng g^{-1} for As, 0.1 ng g^{-1} for Cd, and 0.6 ng g^{-1} for Pb.

The soil solution concentrations of As, Cd and Pb were determined based on a soil-to-water ratio of 1:0.5 (w/v) as outlined in Chen et al. (2007b). The soil and water mixtures were allowed to equilibrate for 48 h on a reciprocating shaker (at 20 rpm), the samples were then centrifuged and the supernatant was decanted and filtered through a 0.45 μm hydrophilic PVDF membrane filter. The As, Cd, and Pb concentrations in the solutions were analyzed by ICP-MS following the procedures proposed by McBride and Spiers (2001).

2.3. Additional data

In addition to the samples we collected, we obtained the California portion of the data set from a nationwide cropland trace element investigation conducted by USDA Soil Survey (Holmgren et al., 1993) through Dr. Rufus L. Chaney, USDA ARS (Beltsville, MD). The data consisted of concentrations of selected trace elements of soils and of crops harvested from the respective sampling sites. The data were used to establish the PUF_{total} of Cd and Pb for root, vegetable and grain crops grown in California.

2.4. Statistical analysis

The SigmaPlot for Windows (version 10, Systat Software inc.) software package was employed for the statistical analysis. The data was first transformed into logarithm form. Then the data was fitted to Gaussian distribution (with three parameters) that:

$$y = a \times \exp\left[-0.5\left(\frac{x - x_0}{b}\right)^2\right] \quad (3)$$

where y is the probability of K_d or PUF at value of x and a is a constant. The cumulative probability distribution of K_d or PUF was predicted based on the mean (x_0) and standard deviation (b) of the population that:

$$F(x) = 0.5 + 0.5\operatorname{erf}\left(\frac{(x - x_0)}{b\sqrt{2}}\right) \quad (4)$$

where $F(x)$ denotes the cumulative probability that $K_d \le x$, or PUF $\le x$.

3. Results and discussion

The K_d and PUF are mathematically defined parameters commonly used in risk assessment to estimate the potentially toxic trace elements in soil solution and plant uptake from the soils, respectively. In the ensuing discussion of results, we characterize the statistical attributes of the these two parameters based on soil and plant tissue samples obtained from production fields of food crops in California and demonstrate probabilistic nature of the K_d and PUF populations.

3.1. Solid–solution partition coefficient (K_d)

The total soil As, Cd, and Pb contents in California croplands we sampled ranged from 5 to 10 mg kg^{-1}, <0.1 to 2 mg kg^{-1}, and 10 to 20 mg kg^{-1}, respectively. While total As, Cd, and Pb contents of the soils appeared to fall into rather narrow ranges, their corresponding solution concentrations could vary by 20+ folds resulting in a population of wide-ranging soil K_d (Table 1). We included the K_d of the polluted soils reported by Sauve et al. (2000) in Table 1 for comparison purpose, as they were used by CDFA for developing the risk-based numerical limits for As, Cd and Pb in inorganic commercial fertilizers (CDFA, 2002). The K_d of the cropland soils in California ranged from 125 to 1780 l kg^{-1} for As, 409 to 14,000 l kg^{-1} for Cd, and 24,500 to 672,000 l kg^{-1} for Pb. In each case, it occupied a narrow band and within the range of respective element reported by Sauve et al. (2000). As a result, the mean, maximum, minimum and other statistical and probability attributes of these two populations were dissimilar. In risk assessment while the representative K_d of these two populations may be similar, the probability therefore risk interpretations would be quite different.

The K_d represents the concentration of the trace element in solid phase that may produce one unit amount in the solution phase (i.e. 1 mg l^{-1}). A smaller K_d value indicates that a smaller amount of the soil-borne element is needed to produce 1 mg l^{-1} of the element in the solution phase thus potentially higher exposure risks. Based on the mean of K_d values, the As in the cropland soils (mean K_d = 606 l kg^{-1}) appeared to be significantly more soluble than the As of the polluted soils included in Sauve et al., 2000 (mean K_d = 13,100 l kg^{-1}). The Cd and Pb in the polluted soils (mean K_d = 2900 and 171,000 l kg^{-1}, respectively) were comparably insoluble as those in the cropland soils (mean K_d = 3010 and 207,000 l kg^{-1}, respectively). For a polluted soil, the higher K_d values such as those for As do not necessarily constitute lower exposure risks since the total concentrations are so much higher that the solution concentrations of the trace elements, $C_{soil\ solution} = C_{total}/K_d$ remain high regardless of the "large" and supposedly protective K_d values. In the polluted soils, there would be a large pool of soluble elements. Once the elements are removed from the solution phase by leaching or plant uptake, the loss in solution pool would quickly be replenished by those in the solid phase.

It has been postulated that the K_d would normalize the variability due to the soil properties such as pH, soil organic matter content, clay content, etc. (Butcher et al., 1989; Jopony and Young, 1994). For a large-scale investigation spanning the growth regions of entire California, it is imaginable that the properties of soils must have varied region by region and, to a lesser extent, sampling site by sampling site. Therefore, it is reasonable to expect that definitive correlation or pattern between the solution concentrations and their corresponding total concentrations of the soils were not observed (Fig. 1).

Under the circumstance, all of the resulting K_d represented the spatial randomness of the production fields. The observations of solution–solid phase partition of trace elements in California cropland soils would be better described by the probabilistic distribution functions (Chen et al., 2007b). The consumer exposures to the toxic elements in the harvest would be distributed according to K_d in this probability density function. In this way, the uncertainties associated with predicting exposure risks to harvests of the cropland can be evaluated.

Table 1
Summary statistics of solid–solution partitioning coefficients, K_d (l kg^{-1}) of soil As, Cd, and Pb in California cropland soils from this research and reported by Sauve et al. (2000)

Element	K_d obtained in this study			K_d reported by Sauve et al. (2000)		
	Mean ± S.D.	Range	Median	Mean ± S.D.	Range	Median
As	606 ± 404	125–1,780	473	13,100 ± 65,100	1.6–530,000	1,830
Cd	3,010 ± 2,440	409–14,00	2,290	2,870 ± 12,000	0.44–192,000	1,410
Pb	207,000 ± 125,000	24,500–672,000	197,000	171,000 ± 304,000	61–2,300,000	102,000

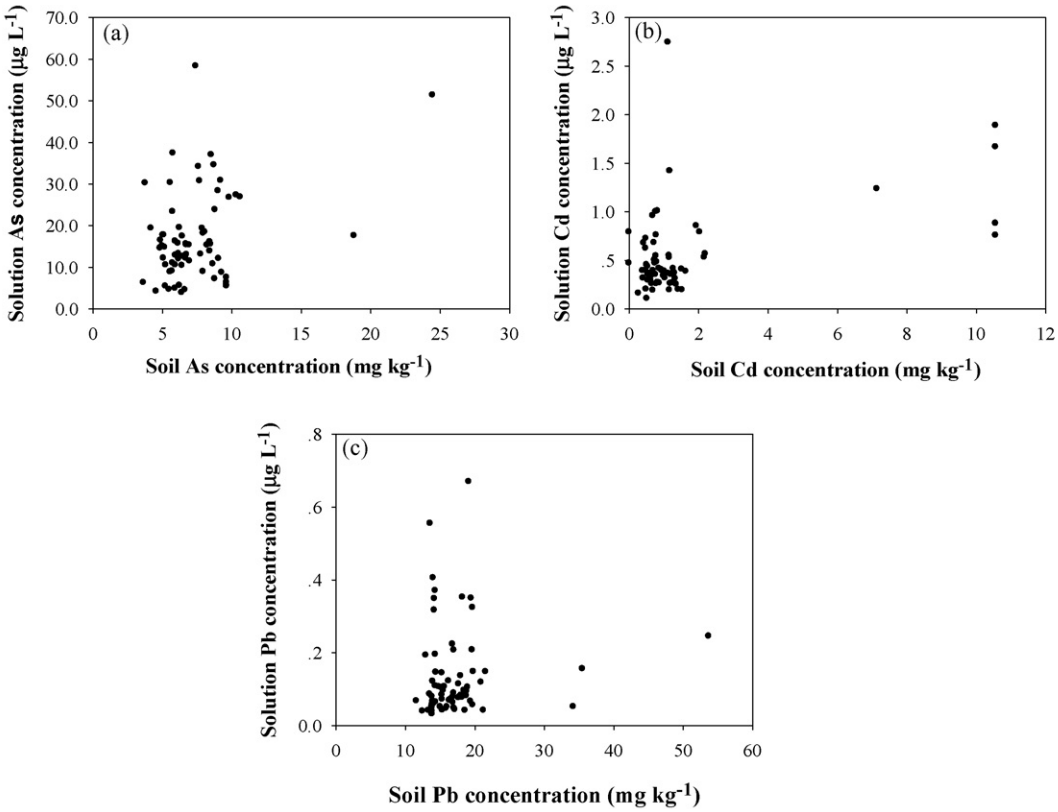

Fig. 1. Distribution of As (a), Cd (b), and Pb (c) between solid and soil solution phases for soils from 70 vegetable fields in California.

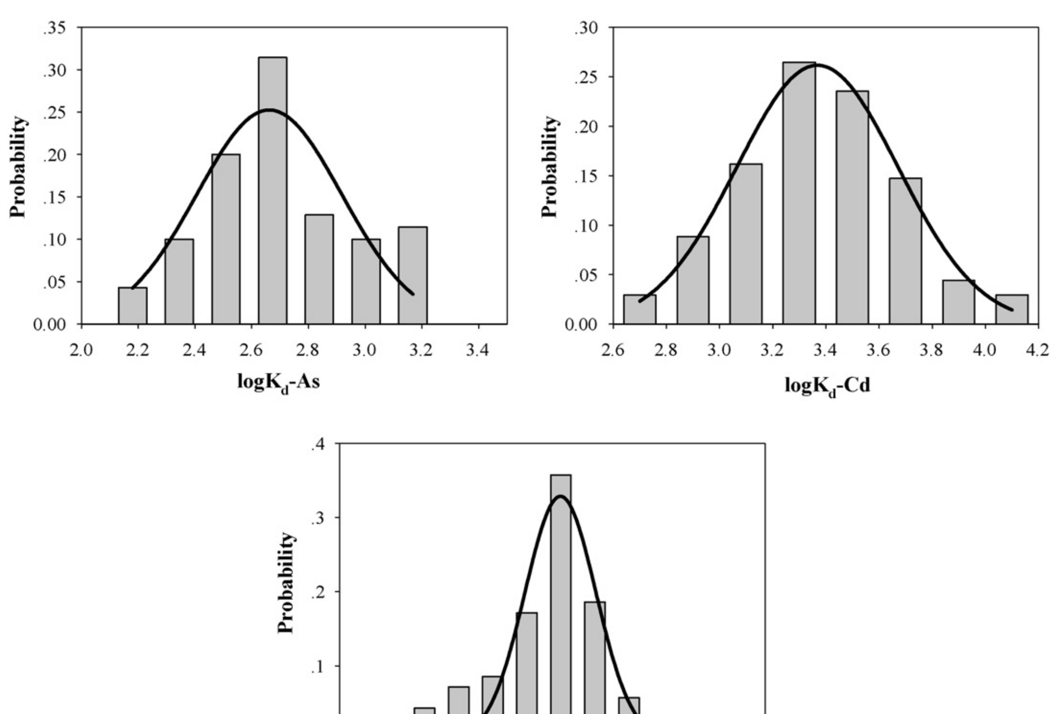

Fig. 2. Probability distributions of K_d of As, Cd and Pb for the soils from 70 vegetable fields in California.

Table 2
Parameters for the probability distribution of partition coefficients (K_d) of As, Cd and Pb in California cropland soils (after logarithmic transformation, fitted to a Gaussian distribution[a]).

Element	Fitted				Measured	
	x_0	a	b	R^2	Mean	S.D.
As	2.66	0.25	0.26	0.675	2.70	0.27
Cd	3.37	0.26	0.30	0.986	3.37	0.31
Pb	5.30	0.33	0.21	0.896	5.22	0.31

[a] The probability function is given by $f(x) = a \times \exp[-0.5((x - x_0)/b)^2]$, a is a constant, x_0 and b are mean and standard deviation of the observed values, respectively.

The K_d values for As, Cd, and Pb of the California cropland soils follow a log-normal probability distribution function (Fig. 2). The means and standard deviations of the probability distributions are in close agreement to those obtained by the experimental data (Table 2). Fig. 3 shows the measured and predicted cumulative probability distribution of K_d for As, Cd, Pb of the California cropland soils. The minimum, mean, upper 95% confidence level and maximum K_d values reported by Sauve et al. (2000) were marked in Fig. 3. The K_d ranges for the cropland soils were well enveloped by the K_d ranges reported by Sauve et al. (2000). In the CDFA study, K_d was not used to estimate the plant uptake of As, Cd, and Pb. Instead, the solution concentrations estimated in this manner were employed to approximate the elemental concentrations in the solution phase and thus the losses through leaching and surface runoff and changes in total trace element contents of the soils. Under this circumstance, the plant uptake factors that were obtained through the total soil element contents of the soils would be sensitive to K_d. It could lead to either under- or over-estimations of the risk from the trace elements in fertilizers if K_d was not representative.

3.2. Predicting the plant uptake, PUF_{total} vs. $PUF_{solution}$

The concentrations of As, Cd, and Pb in plant tissue harvested during this study were comparable to those reported in the literature (Kabata-Pendias and Pendias, 2001) and did not appear to correlate with the corresponding soil solution concentrations (Fig. 4). The resulting $PUF_{solution}$ was summarized in Table 3. For As, the soil solution concentrations ranged from 5 to 40 $\mu g\, l^{-1}$ while the As in the majority of the corresponding plant tissue was less than 0.1 mg kg^{-1}, resulting in a $PUF_{solution}$ range of 0.8–68 l kg^{-1}. For Cd, the soil solution concentrations ranged from near 0 to 3 $\mu g\, l^{-1}$, while the corresponding plant tissue concentrations were as high as 5 mg kg^{-1}, resulting in a $PUF_{solution}$ range of 19–33,500 l kg^{-1}. For Pb, the soil solution concentrations in the majority of the test soils were <0.2 $\mu g\, l^{-1}$, while the concentrations of the corresponding plant tissues varied from near 0 to as high as 3 mg kg^{-1}, resulting in a $PUF_{solution}$ range of 181–68,300 l kg^{-1} (Table 3). Judging from the distributions, the $PUF_{solution}$ appear to be probabilistic rather than deterministic over the range of soil solution concentrations the data defined.

The trace element concentrations of the soil solutions often are not determined. Under such circumstances, PUF_{total} instead of $PUF_{solution}$ had been employed to estimate the elemental transfer potential from soil to plant tissue (U.S. Environmental Protection Agency, 1992; CDFA, 1998, 2002). As the correlations with the soil solution concentrations, the plant tissue concentrations of As, Cd, and Pb were poorly correlated with the total soil contents. The

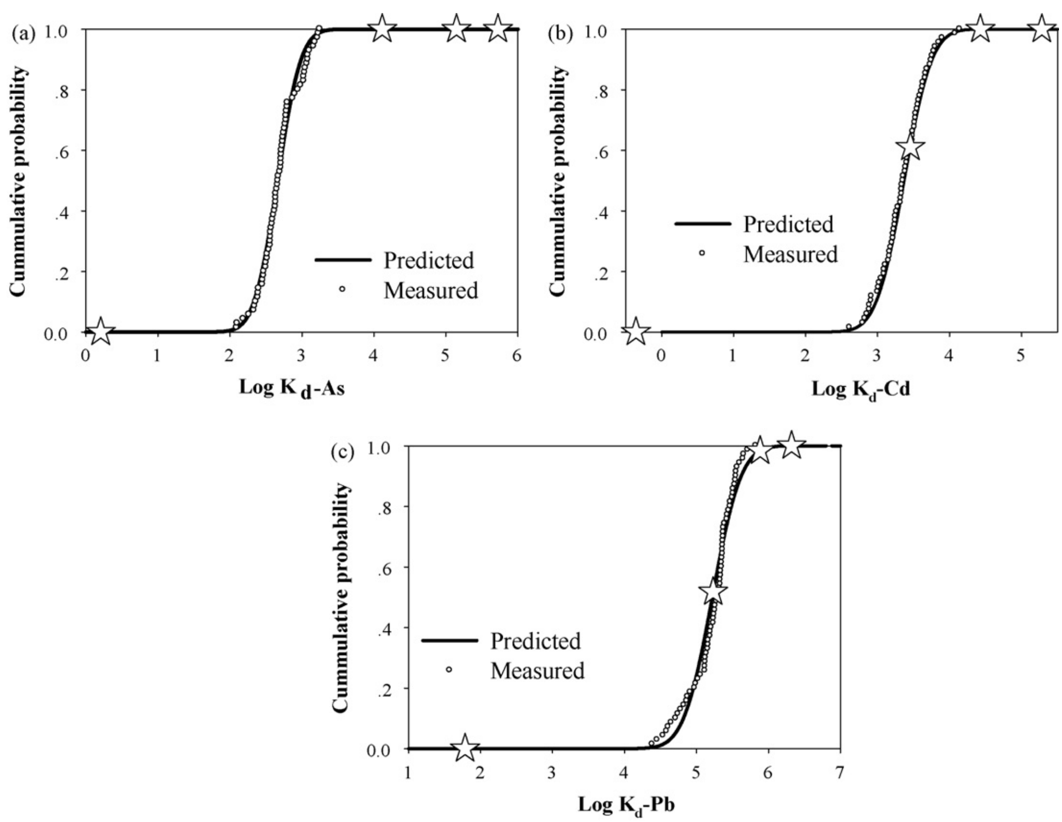

Fig. 3. Measured and predicted cumulative probability distribution of K_d for soils from 70 vegetable fields in California; the asterisks (☆) in the same figure from the left to right refers to the minimum, mean, upper 95% confidence level and maximum K_d used by CDFA, respectively, for (a) As; (b) Cd; and (c) Pb.

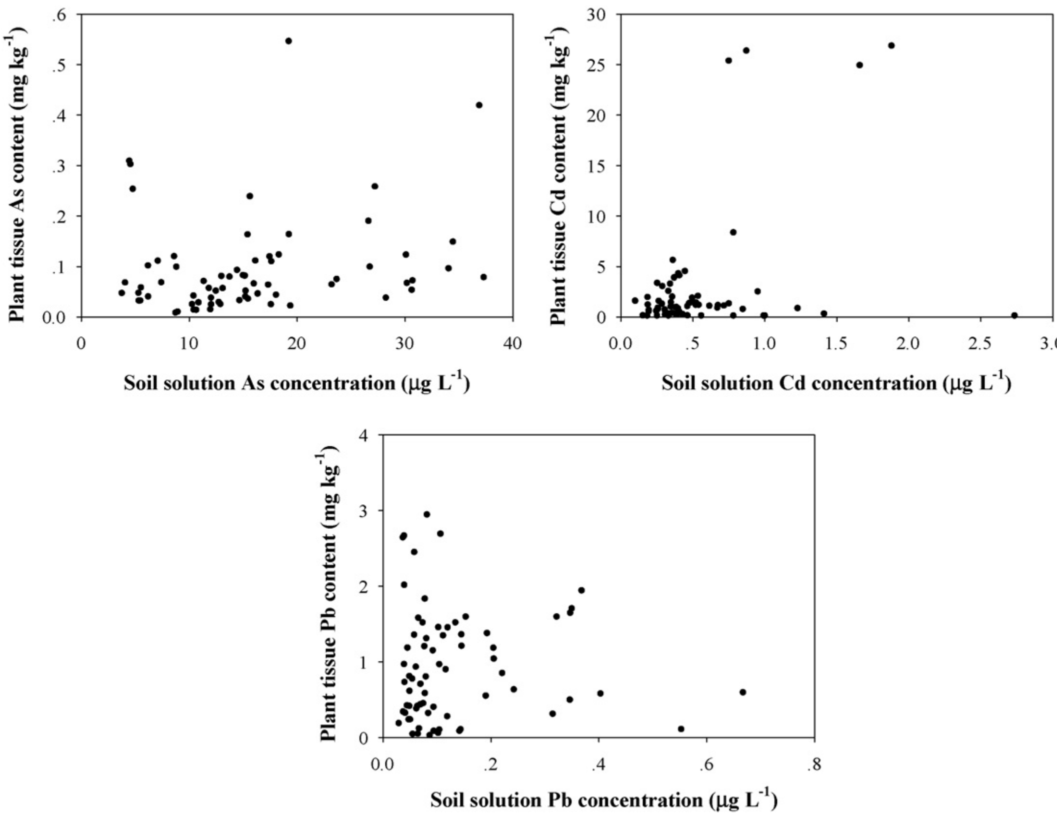

Fig. 4. Relationships between soil solution concentrations and plant tissue concentrations of As, Cd and Pb for the soils from 70 vegetable fields in California.

PUF_{total} we obtained (Table 4) were similar and in same value ranges as the PUF_{total} reported by CDFA (2002). Given that the soil solution is cumbersome to obtain and element concentration of the soil solution is often too low to be determined with routine analytical methods, the $PUF_{solution}$ did not appear to have a distinctive advantage over PUF_{total} as a predictor of trace element transfers from the soils the plants.

There have been attempts to correlate the plant uptake with chemically identifiable fractions of trace element in soil (Singh and Kristen, 1998; McBride, 2002, 2003; Adams et al., 2004; Huang et al., 2004; Kuo et al., 2004). The outcomes however were not conclusive as much of the correlations were not generalized. Our investigation pointed out that neither the total soil content nor soil solution concentration was an accurate predictor for the transfer of a trace element from soil to plant tissue. The distributions of K_d and PUF characterizing transfers of trace elements from soils to plants were probabilistic in nature. The conventional approach of treating PUF or K_d as deterministic parameters overlooked the spatial and temporal variability of transferring trace element across the soil–water–plant system.

In late 1970s, U.S. Soil Survey initiated a nationwide survey of trace elements in cropland soils and their corresponding crop harvests (Holmgren et al., 1993). The PUF_{total} based on California's portion of the data consisted of 2709 observations (Table 5) and would be representative for the purpose of risk assessment. For different plants, the species with higher PUF has a tendency to uptake greater amounts of trace element from one unit concentration of the element in the soil than the one with lower PUF. For the same species, the element with greater PUF is more susceptible to plant uptake than the element with smaller PUF. The PUF_{total} in Table 5 represented elemental transfers from the soils to the edible plant parts. The data illustrated that the uptake potentials of leaf crops and root crops generally are greater than those of the grain crops. Comparing the data in Tables 4 and 5, it appeared that the PUF_{total} used by CDFA were similar in magnitudes and covered the

Table 3
Summary statistics of the $PUF_{solution}$ ($l\,kg^{-1}$) measured from the plant tissues collected from 70 fields in California

Element	Mean	S.D.	Min	Max	Median
As	8.2	12.5	0.8	67.9	4.5
Cd	4510	6320	19	33,500	2140
Pb	11,400	13,600	181	68,300	7330

Table 4
The means and ranges of PUF_{total} for different crops used in the CDFA risk-based study (CDFA, 2002) and obtained by this study

Element	PUF_{total}, employed in CDFA (2002)			PUF_{total}, obtained in this study		
	Root	Vegetable	Grain	Root	Vegetable	Grain
As	0.011 (0.0007–0.10)[a]	0.024 (0.0015–0.36)	0.020 (0.0044–0.06)	–	0.013 (0.0012–0.069)	0.022 (0.005–0.055)
Cd	0.308 (0.005–5.7)	0.68 (0.004–13.3)	0.092 (0.0005–2.5)	–	1.77 (0.11–8.71)	0.22 (0.025–1.29)
Pb	0.026 (0.0013–0.83)	0.014 (0.0001–0.39)	0.0096 (0.0001–0.18)	–	0.052 (0.001–0.21)	0.084 (0.045–0.13)

[a] Numbers in parentheses after means indicate the ranges of the parameters.

Table 5
Summary statistics of the PUF_{total} of Cd and Pb for root, vegetable, and grain crops grown in California (based on data provided by Dr. Rufus L. Chaney)

Crop	Cadmium			Lead		
	Mean	Range	*n*	Mean	Min	*n*
Potato[a]	1.05	0.029–6.28	305	0.007	0.0004–0.367	305
Peanut[a]	2.41	0.13–32.00	320	0.002	0.0001–0.033	306
Onion[a]	0.27	0.23–2.22	255	0.007	0.047–0.577	255
Tomato[b]	1.76	0.17–32.00	182	0.003	0.0001–0.064	179
Cabbage[b]	0.77	0.028–5.38	206	0.008	0.0008–0.122	206
Lettuce[b]	1.55	0.061–12.54	145	0.036	0.0002–0.485	145
Sweet Corn[c]	0.088	0.004–1.18	244	0.003	0.0001–0.043	252
Soybean[c]	0.39	0.046–7.50	339	0.004	0.0002–0.027	338
Wheat[c]	0.21	0.014–1.38	315	0.004	0.0001–0.04	298
Corn[c]	0.15	0.003–4.20	256	0.003	0.001–0.4	281
Rice[c]	0.13	0.003–3.40	142	0.001	0.0001–0.007	148
Root crops	1.32	0.029–32.00	880	0.005	0.0001–0.577	866
Vegetable crops	1.32	0.028–32.00	533	0.014	0.0001–0.485	530
Grain crops	0.21	0.003–7.50	1296	0.003	0.0001–0.400	1317

[a] For the purpose of this study, they are considered as root crops.
[b] For the purpose of this study, they are considered as vegetable crops.
[c] For the purpose of this study, they are considered as grain crops.

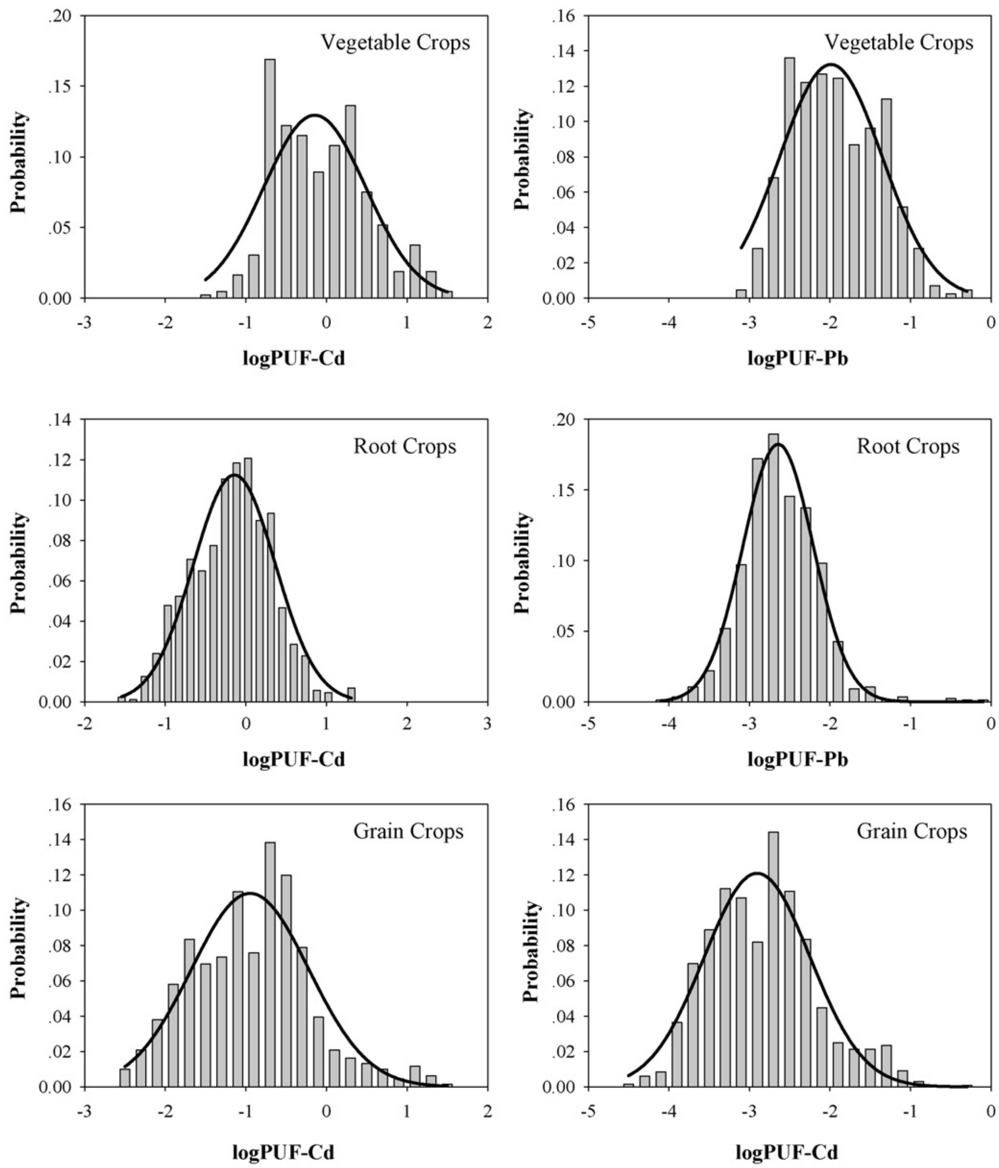

Fig. 5. Probability distributions of PUF_{total} of Cd and Pb for the vegetable, root and grain crops (based on data provided by Dr. Rufus L. Chaney).

Table 6
Parameters of the log-normal probability distribution of PUF_{total} of Cd and Pb for the vegetable, root and grain crops

Crops	Cadmium			Lead		
	x_0[a]	b[b]	R^2	x_0[a]	b[b]	R^2
Vegetable	−0.145 (−0.062)	0.633 (0.583)	0.71	−1.99 (−1.93)	0.635 (0.534)	0.85
Root	−0.142 (−0.172	0.509 (0.496)	0.93	−2.64 (−2.62)	0.436 (0.466)	0.98
Grain	−0.947 (−0.932)	0.730 (0.734)	0.85	−2.90 (−2.84)	0.652 (0.667)	0.91

[a] Numbers in parentheses refer to the logarithmic mean of the data set.
[b] Numbers in parentheses refer to the standard deviation of the data set (after logarithmic transformation).

similar value ranges as the PUF_{total} derived from soil and plant tissue samples obtained by Holmgren et al. (1993).

The PUF_{total} of food crops followed log-normal distributions and covered a range spanning approximately 3 orders of magnitude (Fig. 5). Parameters characterizing the probability density functions were summarized in Table 6. Similar to K_d, the cumulative probability distribution of PUF_{total} for each category of food crops can be obtained based on Eq. (4) (Fig. 6). The probabilities of the minimum, mean, and maximum PUF_{total} used in the CDFA risk assessment were calculated and marked on Fig. 6. The PUF_{total} used in the CDFA risk assessment were comparable to patterns observed in the field measurements. It affirms that CDFA's numerical limits for As, Cd, and Pb in inorganic fertilizers were based on valid data.

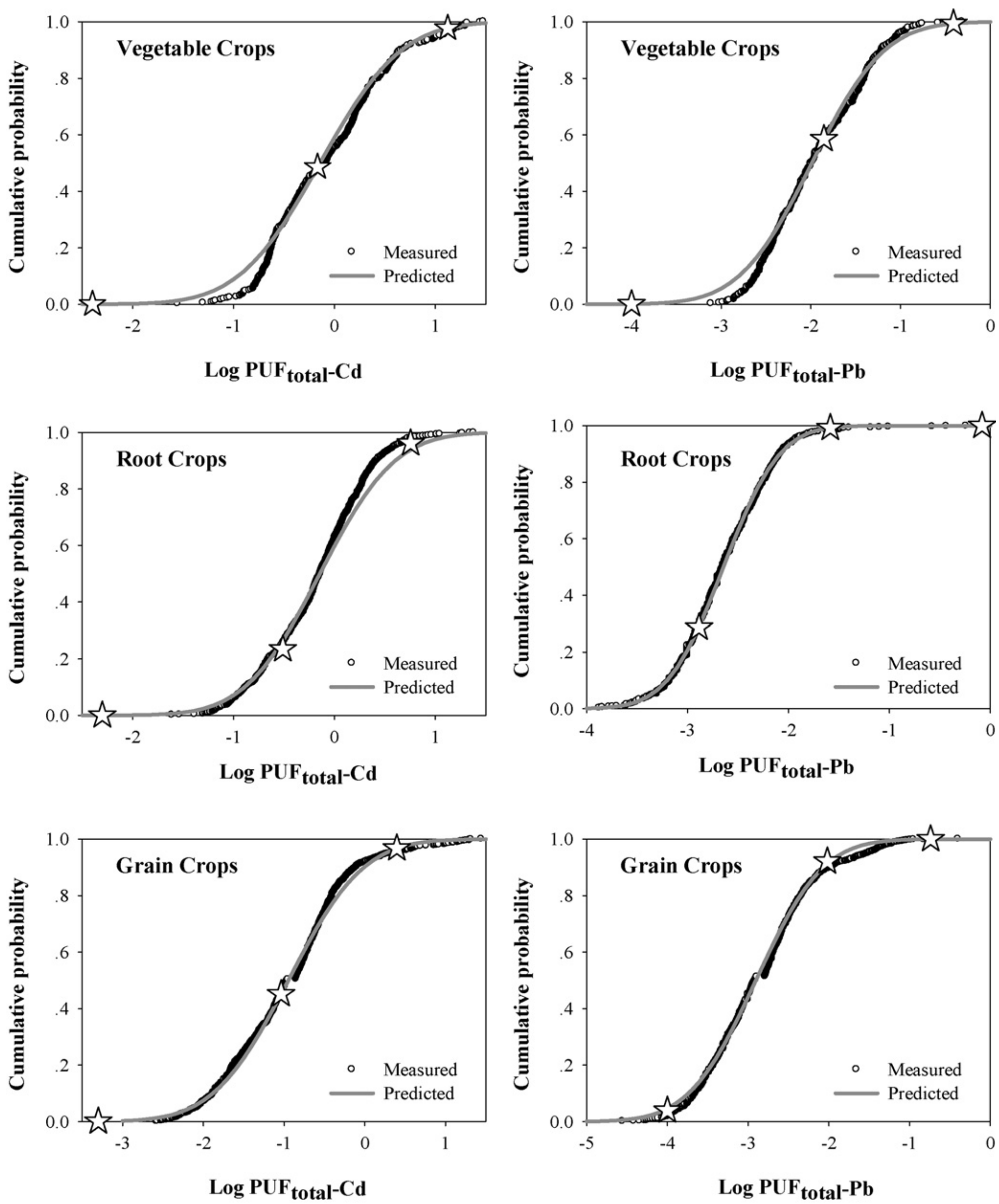

Fig. 6. Measured and predicted cumulative probability distribution of Cd and Pb for the vegetable, root and grain crops (based on data provided by Dr. Rufus L. Chaney). The asterisks (☆) in the same figure from the left to right refers to the minimum, mean, and maximum PUF value used by CDFA, respectively.

4. Conclusions

Soil and plant tissue samples were collected from 70 vegetable fields in California to determine their As, Cd, and Pb concentrations. The experimental data, along with the California's portion of a dataset derived from a USDA nationwide survey of trace elements in cropland soils was used to assess the relationship between As, Cd, and Pb in soil solid and solution phases, K_d, and their effects on plant uptake in terms of the elements in solution phase and solid phase namely $PUF_{solution}$ and PUF_{total}, respectively.

(1) The K_d and PUF for cropland soils are probabilistic in nature and follow log-normal distributions.
(2) $PUF_{solution}$ is not necessarily a more accurate predictor of plant uptake than the PUF_{total}. The PUF_{total} appeared to be a reasonably consistent parameter for estimating plant tissue concentrations given the fact that two sets of independently derived data exhibited comparable results.
(3) The K_d values for the California cropland soils are confined to a much narrower range (approximately within 2 orders of magnitude) than those used in the CDFA risk assessment study (up to 5 orders of magnitude). Using a much wider range of K_d than those could occur in California croplands, the environmental and public health risks associated with the anthropogenic sources of trace elements in soils (fertilizers and other soil amendments) may be over-estimated.

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